UNDERSTANDING QUANTUM YIELDS IN NAPHTHALENES AND BORON-DIPYRROMETHENES: TOWARDS A PREDICTION OF NON-RADIATIVE DECAY PATHWAYS IN ORGANIC OPTOELECTRONIC MATERIALS

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In recent years, organic optoelectronic materials have attracted considerable attention due to their ease of production and fabrication and great potentials in industrial applications. However, their efficiencies can be strongly limited by non-radiative decay pathways in which the excited energies are lost in the form of thermal energy. In the present study, we focused on two families of organic optoelectronic materials, the derivatives of naphthalene and those of boron-dipyrromethene (BODIPY), and characterized their efficiencies using the fluorescence quantum yield (ϕ_{fl}) – the probability that a photoexcited molecule fluoresces a photon rather than undergoing a non-radiative decay. To predict these ϕ_{fl}'s, we developed inexpensive, accurate and transferable semi-empirical methods based on time-dependent density functional theory (TDDFT) and its multiple variants, and examined two non-radiative decay mechanisms – internal conversion (IC) and intersystem crossing (ISC). We managed to predict radiative rates (k_{fl}), IC rates (k_{IC}), and ISC rates (k_{ISC}), and controlled the mean absolute error (MAE) within 0.4 orders of magnitude. These results, in combination, allowed us to reproduce ϕ_{fl}'s with an MAE of 0.2 for organic optoelectronic materials in question. During this process, we discovered two novel IC pathways through low-energy distorted transition states and intermediates, and indicated that the energy gap law is inadequate to estimate the activation energy (E_{a}) and account for k_{IC} and k_{ISC}. The present study paves the way for the rational design of organic optoelectronic devices by high-throughput computations.